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Relation of Copper-Containing Fungicides to the Ascorbic Acid and Copper Content of Tomato Juice

W. B. Robinson, W. T. Schroeder, Elmer Stotz,
and Z. I. Kertesz

NEW YORK STATE AGRICULTURAL EXPERIMENT STATION
Cornell University
GENEVA, NEW YORK

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ABSTRACT

A SERIES of tests with tomatoes sprayed with copper-containing fungicides indicated that the copper content of juice made from the fruit contained an increased proportion of copper over unsprayed fruit.

Thorough washing with water usually removed a considerable proportion of the spray residue copper. Peeled tomatoes from sprayed lots still showed a significant increase in copper content over the fruit from the control lots, indicating that some of the copper finds its way into the fruit proper.

The use of copper equipment will result in an increase in the copper content of the juice, and it is suggested that copper might be picked up by the product if copper-containing alloys are at any time in contact with the juice.

These experiments confirmed the observation that the detrimental effect of copper in tomato juice on the ascorbic acid content is restricted to the period of preparation and processing, and that copper present in the juice has no effect on the loss of ascorbic acid during storage in the closed can. The storage temperature is apparently the principal factor governing the loss of ascorbic acid during storage.

Some of the copper contained in the juice at the time of manufacture is plated out on the inside surface of the can. Inasmuch as the main detrimental effect of the copper content on the behavior of ascorbic acid is during processing, this "loss" of copper has no particular significance from this standpoint. On the other hand, it is clear that copper determinations on stored tomato juice will give results which will not indicate the copper content of the juice during the period when the copper had a detrimental effect on the ascorbic acid content.

No significant effect of copper derived from sprays on the flavor and color of the juice could be observed.

Bulletin No. 725

RELATION OF COPPER-CONTAINING FUNGICIDES TO THE ASCORBIC ACID AND COPPER CONTENT OF TOMATO JUICE

W. B. ROBINSON, W. T. SCHROEDER, ELMER STOTZ, AND Z. I. KERTESZ

INTRODUCTION

THE detrimental effects of high copper content in foods have been recognized for many years. In tomato juice and concentrates, for example, the rapid deterioration of color and flavor and the loss of ascorbic acid often have been thought to be associated with excessive concentrations of copper in these products. In 1940, Great Britain introduced a regulation that tomato products should not contain in excess of 50 p.p.m. of copper on the dry matter basis. This regulation and the possibilities of similar restrictions in this country have further intensified the efforts of tomato growers and processors to keep the copper content of tomato products as low as possible.

While the use of copper and copper alloy equipment have been greatly reduced in plants manufacturing tomato products, a further potential source of copper is from the residues of insecticides and fungicides which contain copper salts. In recent years, frequent and heavy losses of tomatoes from diseases have resulted in the application by many growers of fungicide sprays or dusts. The recommended schedules involve the use of copper-containing fungicides in at least part of the applications, and as a result, processors have been concerned over the possibility of increasing the copper content of tomato products. The present investigations were designed to determine the manner in which copper finds its way into such products as a result of cultural and processing practices, and to study the effects of various amounts of copper on tomato juice.

The work reported in this bulletin dealt with the following problems: (A) Spray residue copper in tomatoes and in tomato juice; (B) effect of copper on the loss of ascorbic acid during the processing and storage of tomato juice; and (C) behavior of the copper in canned tomato juice.

REVIEW OF THE LITERATURE

The copper content of tomatoes and tomato products reported by various investigators are shown in Table 1. Horner (7)[1] stated that tomatoes grown on soil where copper-sprayed tomatoes had been grown previously had a much higher copper content. He found that the use of copper kettles in the manufacture of tomato puree caused an increase of 24 p.p.m. of copper on the dry-weight basis. When stainless steel equipment was used, there was no increase and the canned tomatoes had the same copper content as the unprocessed fruit. In other experiments Horner (8) showed that the addition of copper to the soil of potted plants increased the copper content of the tomato fruit. Wiping the leaves of the plants with bordeaux mixture at weekly intervals during the growing season also increased

TABLE 1.—COPPER CONTENT OF TOMATOES AND TOMATO PRODUCTS.

PRODUCT	CU CONTENT IN P.P.M. ON DRY-MATTER BASIS	INVESTIGATOR	SOURCE OF PRODUCT
Whole fresh tomatoes, untreated soil	7–24	Horner (7)	England
Whole fresh tomatoes, high copper soil	30–40	Horner (7)	England
Fresh tomatoes	8–17*	Tocher (24)	England
Whole tomatoes	15–25	Shannon & Englis (22)	Illinois
Fresh fruit, free of skin and core	6–45	Cockburn & Herd (4)	England
Fresh tomatoes	16–52	Piegai (18)	Italy
Whole tomatoes	17	Remington&Shiver(19)	South Carolina
Whole tomatoes	10–24	Weber & McLean (25)	New Jersey
Canned whole tomatoes, without skin	20–37	Horner (8)	England
Canned whole tomatoes, with skin	25–67	Horner (8)	England
Canned whole tomatoes	24–446	Piegai (18)	Italy
Tomato juice	6–45	Cockburn & Herd (4)	England
Tomato puree	15–47	Horner (7)	Canada
	4–305	Horner (7)	France
	16–38	Horner (7)	Hungary
	21–102	Horner (7)	U. S. A.
	20–230	Horner (7)	Italy
	18–40	Barskii (1)	Hungary
	70–150	Cockburn & Herd (4)	France
	40–250	Cockburn & Herd (4)	Italy
	30–200	Cockburn & Herd (4)	Canada
	30–60	Cockburn & Herd (4)	Austria
	60–200	Cockburn & Herd (4)	Hungary
	120–240	Cockburn & Herd (4)	Bulgaria
	30–120	Cockburn & Herd (4)	U. S. A.

* Approximate; dry weight not given but assumed to be 6 per cent. 1 p.p.m. on dry-weight basis = 0.006 mg per cent on fresh weight basis.

[1]Refers to Literature Cited, page 17.

the copper content of the fruit from 22 to 47 p.p.m. On the other hand, Shannon and Englis (22) found that two dustings of monohydrate copper sulfate during the growing season had no effect on the copper content of the tomato fruit.

Copper has been reported to cause detrimental flavor and color changes in tomato products. Barskii (1) developed a method for evaporating tomato puree whereby he reduced the copper content from "the usual" 40 p.p.m. to between 18 and 31 p.p.m.

Lamb and Lloyd (13) concluded that the natural copper content of tomatoes could be over 30 p.p.m., and that even with slight and moderate copper contact, there appears to be an appreciable contamination and a sufficient amount to exceed the limit set in Great Britain.

Ozetskii and Kefer (16) found that in making tomato purees, the greatest increase in copper content occurs in the pulping process, especially if the metallic containers were not thoroughly polished.

More recently, Clifcorn and Peterson (3) studied the effect of copper on the ascorbic acid content of raw tomato juice at 60° C (140° F) in the presence of excess air. They found that ascorbic acid was lost in direct proportion to the amount of copper in the juice and warned manufacturers against the use of copper equipment in their plants. It is of interest to note in this connection that even the most recent equipment made in this country for the manufacture of tomato products includes some brass parts.

Lamb (12) showed that the addition of 0.5 mg per cent of copper to tomato juice accelerated the destruction of ascorbic acid in aerated samples. In deaerated juice, the added copper had no effect after the initial holding period.

ANALYTICAL PROCEDURES

Copper.—The wet ash method developed by Brenner and Harris (2) was used for all copper determinations. A 10- to 25-gram sample of tomato juice, depending on the copper content, is transferred to a Kjeldahl flask with the aid of double-distilled water. Ten ml of concentrated nitric acid are added and the mixture boiled until brown fumes are evolved. At this point, 3 ml of concentrated sulfuric acid are introduced and the flask heated until brown fumes cease to evolve and charring commences. It is important to follow this direction concerning the lack of formation of brown fumes to avoid explosive mixtures at later steps in the method. Now 2 ml of 70 per cent perchloric acid are added, and the organic material is decomposed almost immediately. The solution becomes colorless or pale straw color. Heating is continued for a few minutes until the excess perchloric acid is volatilized as indicated by the cessation of dense white fumes and formation of a characteristic condensation ring of sulfuric acid. It is important that all the perchloric acid be driven off to avoid interference with subsequent steps. A blank digestion is carried out at least once to correct for possible traces of copper in the reagents.

For the copper determinations, a modification of Haddock and Evans' method (6) was used. After the acid solution cools, approximately 20 ml of double-distilled water are added to the Kjeldahl flask, mixed, and the contents transferred quantitatively to a 125-ml separatory funnel. The flask is rinsed with successive small portions of water until a total volume of about 50 ml is reached in the funnel. Five ml of 15 per cent citric acid, then 5 drops of 0.04 per cent thymol blue indicator are added. A 1:1 solution of ammonium hydroxide is added until a clear blue color is obtained. The total volume should be made to about 70 ml, if not already at this volume.

To the separatory funnel, 10 ml of a 0.1 per cent solution of sodium diethyl-dithiocarbamate are added. The solution is shaken vigorously with 10 ml of carbon tetrachloride, and the carbon tetrachloride layer is separated by running through a filter paper into a 25-ml volumetric flask or glass-stoppered graduated cylinder. The extraction is repeated with successive 5-ml portions of carbon tetrachloride until the lower layer is colorless. Normally three, or at the most four, extractions suffice. The extract is made to volume and read in a photoelectric colorimeter at 420 millimicrons. Construction of a standard curve is made with the aid of a standard copper solution prepared by dissolving copper wire in nitric acid. Standards should be repeated whenever new reagents are required.

The copper content of the soil from both locations was obtained by shaking 100 grams of air-dry soil for 1 hour with 200 ml of 1N sodium chloride. The supernatant liquid was filtered, and a 100-ml aliquot was used for copper analysis.

Ascorbic acid.—Samples of processed tomato juice were withdrawn immediately upon opening of the cans. Five ml of juice were added to 10 ml of 5 per cent metaphosphoric acid. The ascorbic acid was determined by the xylene extraction method (20).

Tomato color.—The extraction method of Kramer and Smith (11) was used to measure the red color of the tomato juice. The density of the benzene extract was determined with a Beckmann quartz spectrophotometer at a wave length of 485 millimicrons.

EXPERIMENTAL RESULTS

SPRAY RESIDUE COPPER ON TOMATOES AND IN TOMATO JUICE

In order to determine the natural copper content of the soil at the two locations where the experiments were to be performed, composite soil samples were collected at both Geneva and Lincoln, N. Y. The copper content of these soils was determined by a sodium chloride leaching process (17), essentially indicating the portion of copper in the soil which may be taken up by plants. The leachable copper contents of the Lincoln and Geneva soils were 4.1 and 5.0 micrograms per 100 grams of soil, respectively. The pH of the Lincoln soil, as meas-

ured by a Beckman glass electrode pH meter, was 5.2, while that of the Geneva soil was 7.4.

In 1944, three different copper fungicides, bordeaux 8–4–100, Microgel (tribasic copper sulfate), and COCS (copper oxychloride sulfate), were applied as sprays to John Baer tomatoes at Geneva and Lincoln. Each treatment consisted of a four-row plot, containing 60 plants, in random order in each of five blocks. Nonsprayed plots served as controls. Each fungicide was used at a concentration equivalent to the application of 4 pounds of copper per acre per application. Four applications were made at each location, beginning about the second week in July and ending during the last week in August. Sprays were applied through a five-nozzle per row boom at the rate of 200 gallons per acre through a No. 3 disc at a pressure of 300 pounds. Disease data and fruit samples were obtained from the two center rows of each plot.

Early blight, *Alternaria solani* (Ell. & Mart.) Jones and Grout, was the predominant disease and accounted for virtually all of the defoliation (Table 2).

For analysis, at least 12 fruits were selected at random from each replicate plot of each treatment, approximately 2 weeks after the last spray application. The tomatoes within each replicate were combined and analyzed in two different manners, viz; (a) the whole fruit was washed with water only as it would be prepared for the

TABLE 2.—THE EFFECT OF VARIOUS COPPER SPRAY TREATMENTS ON THE COPPER CONTENT OF TOMATO FRUIT AND DISEASE CONTROL AT GENEVA AND LINCOLN, N. Y., 1944.

COPPER SPRAY MATERIAL*	PERCENTAGE EARLY BLIGHT DEFOLIATION			COPPER CONTENT OF FRUIT IN MG PER CENT					
				Washed			Peeled		
	Geneva	Lincoln	Av.	Geneva	Lincoln	Av.	Geneva	Lincoln	Av.
None	83	97	90	0.147	0.051	0.099	0.100	0.057	0.078
Bordeaux	31	50	41	0.178	0.106	0.142	0.120	0.083	0.102
Microgel	50	50	50	0.197	0.184	0.190	0.130	0.133	0.132
COCS (44 per cent Cu)	51	56	53	0.160	0.115	0.137	0.124	0.093	0.109
L.S.D. (19:1)†	3	5	3	NS	0.052	0.034	NS	0.043	0.022

* Bordeaux 8-4-100; Microgel, tribasic copper sulfate (50% Cu); COCS, copper oxychloride sulfate (44 per cent Cu).

† Least difference required for significance (odds 19:1). NS indicates no significant difference by analysis of variance.

manufacture of juice or concentrate, and (b) samples were steamed in the laboratory and the skins and cores removed by knives as is done in the preparation of canned tomatoes. The prepared samples were then homogenized in a Waring Blendor and about a pint jar full of this mixture was preserved in frozen storage for the copper analysis.

The results of copper determination on these samples are shown in Table 2. In all sprayed treatments the washed tomatoes had a higher copper content than did the washed and peeled tomatoes. In the case of the nonsprayed plots, the differences between the peeled and unpeeled tomatoes were not considered statistically significant.

In the Lincoln experiment, every comparison both with peeled or washed tomatoes showed the sprayed tomatoes to be significantly higher in copper than the nonsprayed controls. The average copper content of the tomatoes from the Geneva control plots was lower than that of the various sprayed plots, following the same trend as that at Lincoln. The difference at Geneva, however, was not significant, largely because of an extremely high reading in one replicate which could not be removed justifiably from the statistical analysis. No explanation can be offered for this discrepancy, although it seems safe to assume that an error must have been made in the spraying or sampling of that plot.

The Microgel-treated tomatoes were highest in copper at both locations. At Geneva, the differences were small, but at Lincoln the Microgel treatment had nearly 4 times as much copper as the control and 50 per cent more than the next highest copper treatments. It is interesting to note that in spite of the higher copper retention in the Microgel treatment, defoliation control was no better than in the bordeaux treatment.

A comparison between the same tests made at Geneva and at Lincoln showed that, with the exception of the Microgel treatments, the Geneva tomatoes showed a higher copper content. It appears from the copper determinations made on peeled tomatoes that a considerable increase in the copper content due to the use of sprays containing copper salts was noticeable in the peeled fruit and that, therefore, the copper contents of both canned tomatoes and tomato juice made from such fruit would have been increased.

In order to obtain more information on this latter point, further tests were performed in 1945.

Tomatoes for processing were obtained from two different experimental fields, one at Auburn and the other at Phelps, N. Y. At Auburn,

one spray schedule involved five applications of COCS, and two others involved (a) two applications of COCS and three of Fermate (ferric dimethyl dithiocarbamate) and (b) three applications of COCS and two Fermate. Sprays were applied at the rate of 200 gallons per acre through a six-nozzle per row boom, using No. 3 discs and a pressure of 400 pounds. Samples of ripe tomatoes were taken to the plant for processing 2 weeks after the last spray application. Unfortunately, the control sample was lost in these tests.

At Phelps, samples were taken from a nonsprayed plot and a plot sprayed four times with Microgel at the rate of 200 gallons per acre per application, with a spray boom identical to that used at Geneva and Lincoln. Samples were taken 5 weeks after the last spray application.

The tomatoes grown at Auburn were processed in plant No. 1, where the tomatoes were steamed before juicing. The juice was brought to 82° C (180° F) and held for periods varying from 10 to 20 minutes in three 600-gallon copper kettles. After the holding period, it was pumped to the filling machine. The holding period depended on the length of time a kettle of juice had to wait before being filled into the cans for processing. Although 15 minutes was the maximum time of holding when the manufacturing process was working smoothly, employees' rest periods, machinery breakdowns, and other interruptions often caused much longer holding periods.

The tomatoes grown near Phelps were processed at plant No. 2, where two 200-gallon stainless steel tanks were used to heat the juice from the crusher-preheater. Since only two tanks with smaller capacity were used, the holding operation required only 5 to 10 minutes.

For the analyses of the whole tomatoes, 50 of the fruits were chosen at random as they were passing along the conveyor belts. These were ground in a Waring Blendor and composited before analysis. Two cans of the processed juice were analyzed in each lot. The copper analyses on the samples are shown in Table 3.

Washing of the fruit at plant No. 1 removed about half of the copper from the tomatoes, but the copper content of the finished juice was quite high, undoubtedly due to the use of copper heating tanks. At plant No. 2, no copper was lost in the washing operation. This may have been due either to less efficient washing or to a difference in the physical condition of the copper on the tomatoes. Here again the copper content of the finished juice was higher than that of the washed fruit. It is the writers' suspicion that the brass fittings or

TABLE 3.—EFFECT OF COPPER-CONTAINING SPRAYS ON THE COPPER CONTENT OF TOMATOES AND OF TOMATO JUICE MADE THEREFROM.

SPRAY SCHEDULE*	COPPER IN MG PER CENT		
	Before washing	After washing	Canned juice
	Plant No. 1		
C - C - C - C - C.....	0.282	0.126	0.216
C - F - F - C - F.....	0.228	0.108	0.414
C - F - C - F - C.....	0.216	0.120	0.276
	Plant No. 2		
None.....	0.084	0.096	0.174
M - M - M - M.....	0.186	0.192	0.288

* C = Copper oxychloride sulfate (44 per cent Cu) at 4.5 lbs./100 gals.; F = Fermate (ferric dimethyl dithiocarbamate) at 2.0 lbs./100 gals.; M = Microgel (tribasic copper sulfate, 50 per cent Cu) at 4.0 lbs./100 gals. Letters indicate the order of spray applications.

the brass shaft of the juicer might be responsible for this since stainless steel tanks were used in this plant. The copper content of the tomatoes used in plant No. 2 was approximately doubled by the spray treatment, but when the results were recalculated on the dry-matter basis, the copper content of the juice made from the sprayed tomatoes (48 p.p.m.) was still just under the limit set in Great Britain (50 p.p.m.).

The day after they were manufactured, these tomato juice samples were subjected to flavor tests by a panel of experienced tasters, but no differences in flavor could be detected between high and low copper juices from the same processing plant. The tests were repeated after 10 months' storage at 21° C (70° F) and 40° C (104° F). At that time the juice samples stored at 21° C were equally good and those stored at 40° C were equally bad.

The ascorbic acid contents of the fresh tomato juice samples shown in Table 4 were not essentially different in the two groups. The three samples made in plant No. 1 contained 13.5, 14.6, and 13.8 mg per cent, respectively, while the two samples in plant No. 2 contained 12.2 and 11.4 mg per cent ascorbic acid, respectively. It may be added here that no differences were observed in these samples in the retention of ascorbic acid in storage at 40° C (104° F) where all lost about 50 per cent in 10 months. The red color contents of these samples also showed no difference in the fresh state or after storage. Obviously, this may not have been true had the juice (and thus the copper content) been concentrated as in the manufacture of tomato concentrates.

EFFECT OF COPPER ON LOSS OF ASCORBIC ACID DURING PROCESSING AND STORAGE OF TOMATO JUICE

The observations in the previous section indicate that while the use of copper-containing sprays and the use of equipment made of copper-containing alloys will increase the copper content of tomato juice, the effect of the increased copper content on the behavior of ascorbic acid and color during storage of the canned juice was not significant.

The increased copper content might be assumed to affect the ascorbic acid content of the juice during two distinct periods; i.e., (a) From the time the tomato is crushed to the time the juice is cooled in the sealed can after processing; and (b) from the completion of the processing until the juice passes through the channels of commerce and is finally consumed.

Clifcorn and Peterson (3) found that in the presence of air, added copper causes the loss of ascorbic acid proportional to the copper present. This agrees with the writers' observations. Going one step further, it was deemed advisable to establish the effect of copper during processing and storage. Copper was added by dissolving C.P. copper sulfate pentehydrate in tomato juice serum and introducing this solution into the cans immediately after filling and prior to the closing. The juice used in these studies was made at plant No. 2 from tomatoes that were grown in the same field with no copper spray treatment.

The copper additions were calculated to supply 50, 100, and 500 p.p.m., respectively, of copper to the juice on the dry-weight basis. Duplicate sample cans were opened the following day for copper as well as for other analyses. The different treatments were then split into two lots, with one lot stored at 21° C (70° F) and the other at 40° C (104° F). The analyses were repeated on duplicate cans after 4, 7.5, and 10 months of storage at those temperatures. The ascorbic acid content of these samples is shown in Fig. 1.

The ascorbic acid level of the finished product was progressively lower with higher additions of copper. The juice samples that received 50, 100, and 500 p.p.m. on the dry-weight basis (0.3, 0.6, and 3.0 mg per cent on the fresh-weight basis) of copper had, respectively, 93, 84, and 70 per cent as much ascorbic acid as did the control 24 hours after processing. As indicated by the curves in Fig. 1, the effect of the added copper on the ascorbic acid occurred only during processing,

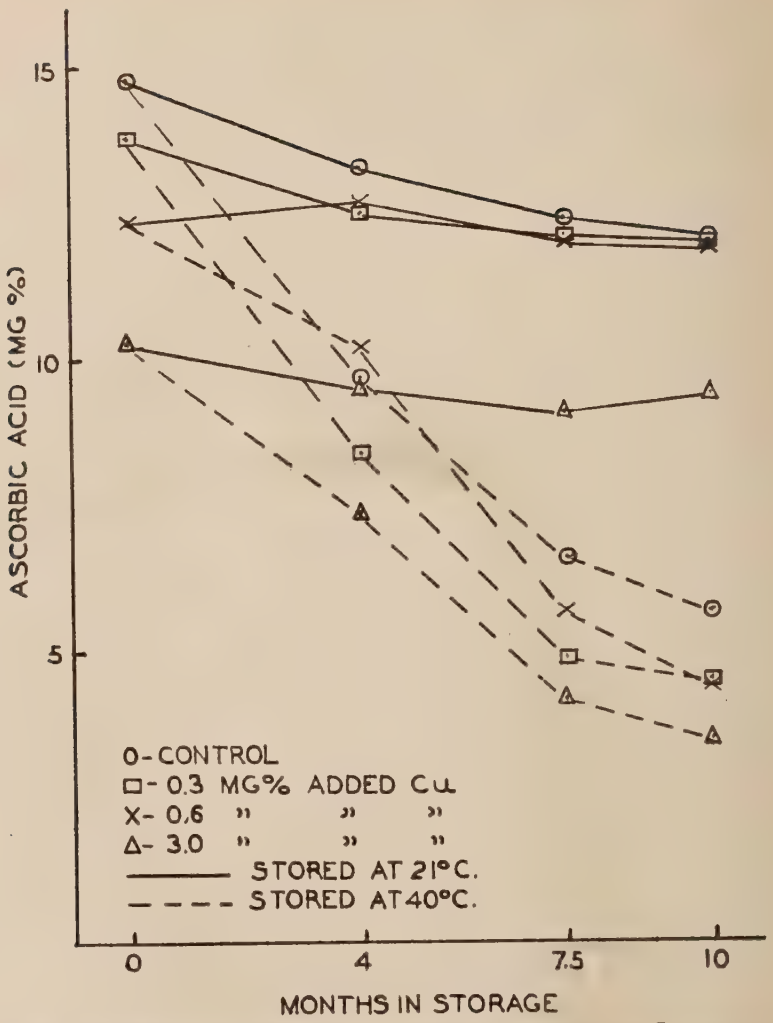

FIG. 1. ASCORBIC ACID LOSSES DURING STORAGE OF TOMATO JUICE CONTAINING ADDED COPPER.

since during storage at either of the two temperatures used the ascorbic acid losses were similar in all the samples.

BEHAVIOR OF COPPER IN TOMATO JUICE

Some analyses of tomato juice samples prepared in 1944 indicated

that the copper content of the canned juice decreases during storage. The preparation of these samples was described by Robinson, Stotz, and Kertesz (21). These samples were prepared by using a variety of "breaking" temperatures. Accordingly, the viscosities of these juices showed considerable variation. These samples were analyzed for copper after 10 months' storage. The results obtained are shown in Table 4.

Table 4.—Effect of "Breaking" Temperature and Storage for 10 Months on the Copper Content of Tomato Juice.

Breaking temperature	Relative viscosity of juice	Copper content, mg per cent after 10 months' storage at		
		0° C (32° F)	21° C (70° F)	40° C (104° F)
90° C (193° F)	2.20	0.165	0.123	0.093
85° C (185° F)	2.02	0.164	0.130	0.124
80° C (177° F)	1.78	0.116	0.103	0.089
71° C (159° F)	1.58	0.114	0.093	0.078
52° C (125° F)	1.58	0.125	0.093	0.089
27° C (80° F)	1.59	0.111	0.087	0.078

The differences in the copper content of the various samples are quite striking. Inasmuch as these samples were all prepared from the same lot of tomatoes which had received no copper spray, the observed differences may be due to two main factors, namely, (a) variations in the amount of copper picked up during manufacture due to the different breaking temperatures used, and (b) to the differences of the loss of copper during storage as affected by the differences in the viscosity of the juice. Unfortunately, no analyses for copper of the original tomato juice samples were available, and, therefore, no conclusive answer can be given to question one. It would not appear that the slight difference from 80° C (177° F) to 85° C (185° F) could make a great difference in the solubility of copper in the juice. On the other hand, as has been shown by Kertesz (9) and Kertesz and Loconti (10), between these two temperatures a sharp line of demarkation is passed between viscous and nonviscous juices, and it seems that the copper retention in the two different types of samples was consistently and significantly different.

To obtain further information on the effect of storage on the copper content of tomato juice, the samples prepared with added copper and already described have been subjected to storage at two different temperatures. The copper analyses af these samples are shown in Table 5.

TABLE 5.—CHANGES DURING STORAGE IN COPPER CONTENT OF JUICE TO WHICH COPPER HAD BEEN ADDED AT VARIOUS LEVELS.

ADDITION OF COPPER IN MG PER CENT	COPPER CONTENT OF FRESHLY CANNED JUICE IN MG PER CENT	COPPER CONTENT IN MG PER CENT AFTER					
		4 months at		7.5 months at		10 months at	
		21° C	40° C	21° C	40° C	21° C	40° C
None	0.102	0.090	0.078	0.084	0.084	0.084	0.066
None	0.120	0.102	0.090	0.108	0.090	0.094	0.088
0.300	0.414	0.414	0.168	0.366	0.270	0.396	0.210
0.600	0.720	0.702	0.630	0.744	0.606	0.672	0.570
3.000	2.886	1.31	1.34	0.906	0.564	0.636	0.498

These samples again show the loss of copper during the storage of tomato juice in the can. The differences due to the storage temperatures are perhaps most striking. When stored at 100° F, over 80 per cent of the original copper content is lost. Naturally, this loss of copper occurs due to deposition on the inside surface of the can. The insides of the cans were rinsed with hot acid followed by analyses of the rinsings. The cans in which the tomato juice "lost" much copper yielded much more deposited copper than did other cans.

DISCUSSION

Factors affecting the copper content of tomato fruit are not well understood. Horner (7) was able to show a relationship between the copper content of the soil and that of the fresh tomato fruit. In the investigations reported herein, the soil at Geneva was found to contain 22 per cent more copper in the sodium chloride leachate than that at Lincoln, while the tomatoes at Geneva were 76 per cent higher in copper. Little is known about the relationship between leachable copper and its availability to the plant. Differences in soil pH, temperature, rainfall, and other factors also may have an effect.

The amount of copper residue remaining on sprayed tomatoes will vary widely with the methods of application and with climatic conditions at the time the spray is applied as well as afterward. The form in which the copper is present in the spray influences the copper retention on the fruit. The copper of the tomatoes at both locations was greatest when applied as Microgel. The copper content of the sprayed tomatoes could be greatly decreased by thorough washing on a commercial scale. This point must be strongly emphasized. If copper spraying is put into wide practice, special attention should

be given to thorough washing of the tomatoes. If the tomatoes are well washed, there is little chance of the copper level in the juice being dangerously high.

Copper which finds its way into tomato juice has the expected detrimental effect on the ascorbic acid content. However, at times the copper content of tomatoes obtained from plants which were not sprayed with copper-containing fungicides might be higher than that of other tomatoes grown on a different soil and sprayed with such fungicides. The oxidation of ascorbic acid caused by copper seems to occur only in the presence of atmospheric oxygen as during heating of the juice in the kettle, while in the cans it is apparently limited by the quantity of oxygen which is either dissolved in the juice or is contained in the head space of the can. Once this oxygen is used up, as during the processing of the canned juice, the amount of copper present has no effect on the loss of ascorbic acid during storage.

The observation that copper is lost from tomato juice during storage in uncoated tin plate cans has little practical significance once the can is processed, since the harmful effects of the copper occur during the manufacture and processing operations. However, the results show that a simple copper analysis of tomato juice that has been stored over any length of time will not be sufficient to indicate the amount of copper that might have been present in the juice at the time of packing and which might have been responsible for loss of ascorbic acid during the manufacturing process.

The studies on the effect of added amounts of copper reported herein confirm the findings of Clifcorn and Peterson (3) and of Lamb (12) in that ascorbic acid losses in the presence of air are proportional to copper content of the juice. During prolonged storage, the copper concentration no longer has an effect on the rate of loss of ascorbic acid.

Although the copper additions reported here had no adverse effect on the lycopene pigment of the tomato juice, MacGillivray's statement (15) that copper causes detrimental color changes is not refuted. Prolonged heating in the presence of air and copper, as during the manufacture of concentrates, may cause the deterioration of color and flavor in addition to enhancing the destruction of ascorbic acid.

SUMMARY

1. The use of copper sprays on tomatoes may increase the copper content of the peeled as well as the unpeeled fruit.

2. Over 50 per cent of the copper of sprayed tomatoes may be removed in the commercial washing process.

3. The use of any copper-containing equipment in the canning process may contribute copper to the finished product.

4. Ascorbic acid retention during processing of tomato juice decreases as the copper content of the juice is increased.

5. The copper concentration has no appreciable effect of the rate of loss of ascorbic acid in the stored canned juice.

6. The copper content of canned tomato juice declines during storage, as it plates out on the inside of the can. The main significance of this fact is that analyses of stored canned tomato juice will not give a true picture of its copper content at the time of manufacture.

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